Evolution of anthropogenic aerosols in the coastal town of Salina Cruz, Mexico: Part I particle dynamics and land–sea interactions

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Abstract

Measurements of aerosol particles in a coastal city in southeast Mexico show that the concentrations and optical properties are strongly linked to land and sea breezes. Maximum concentrations of condensation nuclei (CN), black carbon (BC) and particle bound polycyclic aromatic hydrocarbons (PPAH) occur during land breeze periods and decrease with the sea breeze. The concentrations of particles in air from the ocean, however, remain significantly above background, maritime values as a result of the recirculation of anthropogenic emissions. The mass size distribution is dominated by particles larger than 5 μm when wind speeds exceed 4 m s⁻¹; otherwise, the uptake of water vapor onto unactivated particles is the process that dominates the growth of particles. Precipitation removes particles larger than 5 μm but CN, BC and PPAH concentrations are minimally affected.

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1. Background

Salina Cruz is a medium sized town situated on the Pacific coast of the Isthmus of Tehuantepec (16.2° N, 95.2° W). The city, with an official population of 230,000, is the southern terminal of the railroad that crosses the Isthmus of Tehuantepec and also serves as a southern port primarily for the products of one of Mexico’s largest oil refineries. The presence of this refinery and its emission of copious quantities of gases and particles was the motivation for a project to measure these contaminants and evaluate their impact on the regional environment, especially related to processing by clouds (discussed in the Part II companion paper).

The presence of the particles from this area was first noticed in 2001 when the C-130 aircraft, operated by the US National Science Foundation, was making measurements in the Mexican Intertropical Convergence Zone (ITCZ) during the 2001 East Pacific Investigation of Climate (EPIC) project (Raymond et al., 2004) in a region approximately 700 km to the south of Salina Cruz. The concentration of condensation nuclei (CN) was four to five times higher when winds were from the direction of southern Mexico than when they were from the west (Baumgardner et al., 2005). Three years later, in February 2004, the same aircraft made measurements much closer to Salina Cruz (http://raf.atd.ucar.edu/Projects/GOTEX/docs.html) and measured a plume...
of particles with sizes larger than 0.05 μm and concentrations greater than 50,000 cm$^{-3}$, 80 km downwind of the city (unpublished data).

The following spring, a research team from the Universidad Nacional Autónoma de México installed a suite of instruments in the city of Salina Cruz to measure the properties of gases and particles during the period June 4–18, close to the source of the pollution seen in previous studies over the ocean. The primary goal of the project was to evaluate the influence of anthropogenic emissions on cloud and precipitation processes and to estimate the effects of cloud processing of pollutants. According to climatological records of this region, the month of June is a period of maximum precipitation.

The measurement site was located in the town of Salina Cruz at the Mexican Oceanographic Research Institute 1 (N 16.178°, W 95.196°). The site was approximately one and a half kilometers north of the waterfront and south of the majority of vehicular traffic in the heavily populated areas. On the northeast border of the town, about 2 km from the measurement site, is a large oil refinery (inset, Fig. 1). As also shown in Fig. 1, the topography of Salina Cruz and the surrounding region is complex with numerous small hills within and around the city. The city is situated at the most southern end of the Isthmus of Tehuantepec, a narrow region that separates the Gulf of Mexico from the Pacific Ocean. In the central part of the Isthmus there lies a 40 km gap in the mountain range. The wind direction and magnitude are a combination of large scale meteorological conditions and topographical features (Romero-Centeno et al., 2003).

The majority of the particles at the research site come from local emissions. A road passes in front of the institute that is heavily used during the day by cars, local buses and large trucks. The majority of the trucks are diesel whereas the buses were a mixture of diesel and gasoline. An additional source of BC was a diesel burning train that passed infrequently on the eastern edge of the research site. Ships in the harbor to the south, less than a kilometer from the site, could also be seen to occasionally emit dark smoke, presumably from diesel engines.

In the following sections we present an evaluation of the evolution of the physical, optical and some of the chemical properties of aerosol particles with respect to meteorological conditions and precursor gases and identify the primary production and growth mechanisms. This paper, Part I of three parts, focuses on particle dynamics. Part II presents an analysis of the chemical composition of the particles and Part III is a modeling study of the air motion in this region.

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1 The research institute is part of the Mexican Navy operation in the Salina Cruz region.
2. Measurement and analysis methodology

Listed in Table 1 are the instruments that were deployed and the atmospheric components that were measured. The local winds were measured with two anemometers. One was located at the research institute, at an altitude of 13 m above sea level (ASL) and the other was on the roof of a hotel at an altitude of 34 m ASL, 120 m to the northeast of the first site. Temperature, relative humidity (RH), pressure and rain rate were only measured by the weather station at the research institute. The recording rates from the weather station at the research institute and anemometer at the hotel were every hour and minute, respectively. The wind data reported in the current analysis will be that from the hotel with the exception of June 3 and 4 (days of the year 155 and 156) when this measurement system was not operating. The wind measurements from the hotel were used because of the higher sampling rate. A comparison of the winds from the two systems showed average wind directions in close agreement and the velocity at the hotel approximately a meter per second higher.

A Differential Optical Absorption Spectrometer (DOAS), that measured daytime, column-integrated SO₂ and NO₂, was located just below the hotel roof. The spectra from the DOAS were recorded once per minute. This instrument, however, was also frequently moved to a different location to measure emissions close to the refinery, so we have chosen to use its measurements in this paper only on a single day to illustrate the recirculation of pollutants, as will be discussed in detail in Section 4.

The measurements from the condensation nucleus (CN) counter (TSI Model 3010), nephelometer (Radiance Research) and particle aerosol soot photometer (PSAP, Radiance Research) were recorded every second. The particles were not dried prior to measurements with the nephelometer nor were corrections made to account for the size truncation at large forward scattering angles. A black carbon (BC) mass concentration was derived from the absorption coefficient, \( B_{\text{abs}} \), using the factory recommended specific absorption coefficient of 10 m \( \mu \text{g}^{-1} \). This conversion factor was applied after the absorption coefficients had been corrected according to Bond et al. (1999) in order to account for differences from factory specifications in deposit area and flow rate and for the effects of light scattering. The mass concentration of particle bound polycyclic aromatic hydrocarbons (PPAH) was recorded every 5 s and the optical particle counter (OPC) generated a size spectrum (six channels) every 6 s. The concentrations from the PPAH real-time analyzer have not been compared with an analytical method, as recommended by the manufacturer. Therefore, the reported values are discussed with respect to relative changes. Diesel emissions are a primary source of PPAH (Miguel et al., 1998); hence, this measurement technique is a very fast response indicator of diesel emissions and in comparison with the derived BC values provides a sensitive tracer for changes in particle composition, as will be discussed in Section 3.2.

Numerous times during the project there were power failures that caused an interruption in the data acquisition. These will be seen as gaps in the time series shown in Figs. 2, 4, and 6.

3. Results

3.1. Meteorological trends

The winds at Salina Cruz follow a daily land/sea breeze pattern and the topography channels the land

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Instrument</th>
<th>Technique</th>
<th>Measurement range</th>
</tr>
</thead>
<tbody>
<tr>
<td>T, P, RH, U, V, rain rate</td>
<td>Meteorological station</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPAH mass</td>
<td>Ecochem PAS-2000</td>
<td>Photoemission of electrons</td>
<td>1–100 ( \mu \text{g} \text{m}^{-3} )</td>
</tr>
<tr>
<td>Particle size distribution</td>
<td>PMS LASAir II</td>
<td>Light scattering from single particle in 680 nm laser beam</td>
<td>Six channels, 0.3–0.5, 0.5 to 1.0, 1.0–5.0, 5.0–15, 15–25 ( \mu \text{m} )</td>
</tr>
<tr>
<td>Condensation nuclei (CN)</td>
<td>TSI Model 3010</td>
<td>Optical particle counter</td>
<td>Condensation nuclei 0.05–3 ( \mu \text{m} )</td>
</tr>
<tr>
<td>Scattering coefficient, ( B_{\text{scat}} )</td>
<td>Radiance Research Nephelometer</td>
<td>Light collection from particles ensemble (( \lambda = 540 \text{ nm} ))</td>
<td>Scattering coefficient, 1–1000 ( \text{Mm}^{-1} )</td>
</tr>
<tr>
<td>Absorption coefficient, ( B_{\text{abs}} )</td>
<td>Radiance Research</td>
<td>Light transmission through a quartz filter (( \lambda = 565 \text{ nm} ))</td>
<td>Absorption coefficient, 1–1000 ( \text{Mm}^{-1} )</td>
</tr>
<tr>
<td>Column SO₂, NO₂</td>
<td>Cenit-sky Differential Optical Absorption Spectrometer (DOAS)</td>
<td>Light absorption of scattered sunlight</td>
<td>280–420 nm</td>
</tr>
</tbody>
</table>
breeze into a direction directly from the north and the sea breeze from due south. The hourly trends in winds, temperature, humidity, pressure and precipitation are shown in Fig. 2 for the 15 day research period. The cosine of the wind direction angle (Fig. 2d) is used to emphasize the northerly and southerly wind directions. The average temperature, RH, wind speed and pressure during the project were 27 °C, 77%, 1.5 m s$^{-1}$ and 1014 mb, respectively. During the research period there was a series of four easterly waves that propagated through the area, as seen in the pressure trends (Fig. 2a) on days 156, 161, 165 and 169. There was heavy rain at the measurement site during the passage of the first three waves (days of the year 156–157, 160–161 and 164) and heavy rain was observed over the Gulf of Tehuantepec during the passage of the fourth wave. The first and fourth wave passages were followed by higher than average wind velocities and temperatures, 3 m s$^{-1}$ and 4 °C, respectively. The relative humidities decreased by almost 20%. The normal wind pattern, when not under the influence of the larger scale disturbance, followed a daily cycle of weak northerly winds that began at approximately 23:00 and continued until late morning the following day when the direction shifted to a southerly sea breeze and the speed increased at approximately 11:00. This pattern is seen in the time series (Fig. 2d and e) and is highlighted by the frequency distribution of northerly and southerly wind events as a...
function of hour shown in Fig. 3b. The wind rose plotted in Fig. 3a shows that the sea breeze is generally much stronger than that from the land, due to the combined effect of the land and sea thermal contrast and the upslope flows in the mountains that surround the city.

### 3.2. Aerosol particle trends

Fig. 4 displays the time series of particle number and mass concentrations, their optical properties and the concentration of PPAH. The data points represent 30 min averages. The mass concentration of particles is estimated from the size distribution measured with the OPC under the assumption that the particles are spherical with an average density of 1.0 g cm$^{-3}$. All particle sizes reported in this paper are diameters. These assumptions presume that particles in the size range measured by the OPC (0.3–25 μm), and in the high humidity environment, as a result of the diffusion of water vapor, are dilute solutions of inorganic or organic compounds. The CN concentration (Fig. 4f) follows a daily cycle with maxima in the morning and early evening. The morning maximum is associated with work traffic when the measurement site is downwind of the highest intensity of emissions. The CN concentration decreases by vertical mixing as the boundary layer grows and traffic density diminishes. The shift to a sea breeze at 11:00 further decreases the CN; however, regardless of the strength or duration of the sea breeze, the concentration is always much higher than normal maritime values that are typically lower than 500 cm$^{-3}$ (Heintzenberg et al., 2000). The concentrations of
particles >0.3 μm, those measured with the OPC, follow a similar daily pattern (Fig. 4e), although there are periods when the double maxima are less distinct than for the CN concentrations. The mass of the particles is dominated by the very large particles, those with diameters larger than 5 μm (Fig. 4d), when the wind exceeds 4 m s\(^{-1}\), as seen on days 157, 158, and 166 through 170.

The trends in the light scattering and absorption coefficients (Fig. 4b and c), \(B_{\text{scat}}\) and \(B_{\text{abs}}\), follow those of the CN and particulate mass (PM) concentrations. The peaks in \(B_{\text{abs}}\) (Fig. 4b) are more sharply defined than those of \(B_{\text{scat}}\). The maximum values in \(B_{\text{abs}}\) correspond to those of CN which indicates that BC particles are a major fraction of CN. The correlation coefficient, \(r^2\), between \(B_{\text{scat}}\) and OPC total concentration is 0.70. This correlation shows that light scattering is dominated by particles larger than 0.3 μm. In addition, the greater variability in the optical parameters indicates that not only primary emissions influence these parameters, but other processes are influencing the size and concentrations of particles in this diameter range.
The PPAH mass concentrations (Fig. 4a) mirror the pattern of $B_{\text{abs}}$. This relationship is expected since PPAH, like BC, in urban areas is produced primarily from the combustion of diesel fuel (Miguel et al., 1998; Richter and Howard, 2000). Gas phase PAH also is strongly adsorbed onto surfaces of BC particles (e.g. Dachs and Eisenreich, 2000); hence, shifting the gas-particle partitioning of PAH to PM.

The local precipitation (solid circles on Fig. 4a), while quite heavy at times, appears to have little impact on either the magnitude or the cyclic pattern of the CN, BC (as represented by $B_{\text{abs}}$) or PPAH. Since these concentrations are dominated by particles in the nucleation size range (<0.1 μm diameter) this suggests that small particles are not scavenged by the rain drops. The exception to this was during days 162 and 163 when the CN concentration was significantly suppressed when compared with adjoining periods; however, neither the PPAH nor $B_{\text{abs}}$ showed this decrease. There was light rain on day 162 (Fig. 4a) but the meteorological record provides no means to judge whether these days were any different than other periods.

The average volume distributions from each of the 15 days had shapes that fit into one of the four pattern types that are presented in Fig. 5. The solid and dashed curves correspond to averages when the winds were from the north and the south, respectively, and greater than 1 m s$^{-1}$. Note that the volume shown in the first size interval from 0.05 to 0.3 μm is derived from the CN concentration after subtracting the total number concentration measured with the OPC. An average diameter of 0.1 μm is assumed for this size interval in the calculation of volume concentration. The four distributions reflect the particle production (Fig. 5a and b) and

Fig. 5. The volume concentrations of particles as a function of size in the range from 0.05 to 25 μm are shown for the four representative conditions during the field project: a) strong winds, b) very strong winds, c) heavy rain and d) low winds no rain.
removal (Fig. 5c and d) processes discussed in the following section.

4. Discussion

The changes in particle properties are correlated with meteorological conditions, concentration of precursor gases and the intensity of primary particle emissions. Size distribution is sensitive to temperature primarily as a result of vertical mixing in the boundary layer. This process decreases the number and mass concentration by dilution; however, many heterogeneous chemical reaction rates are also temperature sensitive and affect diffusional growth. The diurnal trend in temperature also drives the land–sea breeze cycle, the most important meteorological factor that changes the distribution of aerosol properties in Salina Cruz.

Fig. 5a is an example when the winds were strong throughout the day. This highlights the production of very large particles, greater than 5 μm. Mechanical production of soil dust and sea salt particles is the primary source of particles in this size range; however, as a result of air mass recirculation, discussed further on, the source of the large particles cannot be strictly attributed to land or ocean sources. Large particles have appreciable deposition (sedimentation) velocities, 0.1–2 cm s⁻¹ (Friedlander, 2000), and have short atmospheric lifetimes. When the rate of production is lower than that of removal, the volume concentration of particles >5 μm will be smaller than particles in the 1–5 μm diameter range. On the day illustrated in Fig. 5a, the nearly constant volume for particles greater than 0.3 μm indicates that the production and removal rates of particles in this size range are approximately the same. This type of average size distribution was found on days 157, 163 and days 166–168. Fig. 5b shows volume distributions from a single day with even stronger winds when the production rate exceeds that of removal, as shown by the increasing volume with size. This behavior is also illustrated in the time series of the PM in particles larger than 5 μm (Fig. 4c).

There are two mechanisms for removing particles from the atmosphere, wet and dry deposition. Wet deposition will remove particles by nucleation scavenging in clouds or by inertial scavenging by precipitation. The largest aerosol particles are removed most efficiently by rain drops (Pruppacher and Klett, 1984; Ducret and Cachier, 1992) because of their larger inertia as shown in Fig. 5e. This size distribution was found on days with precipitation, 155, 156, 160, 161 and 164. The volume concentration of particles larger than 5 μm is more than an order of magnitude lower than those smaller in diameter. This was a period with heavy rain throughout most of the day. The concentration of the smallest particles, 0.05–0.3 μm, appears to be little affected. Their volume concentration is nearly the same as when the winds are high (Fig. 5a and b). This was also seen in Fig. 4a, b and f where the CN, absorption coefficients and PPAH concentration showed no changes during the precipitation.

Dry deposition also preferentially removes the largest particles as a result of their mass and inertia that increases the deposition. The volume of the particles larger than 5 μm, shown in Fig. 5d, is an order of magnitude less than the volume concentration of smaller particles. These measurements were made on a day with no precipitation and mean wind velocity of 2 m s⁻¹.

Particles very near the emission sources will grow by collision and coagulation; however, dilution rapidly decreases the total concentration and diminishes the importance of this growth process once the particles are a few meters away from the source. Diffusional growth is the dominant process that changes the distribution of particle mass. The RH was almost always above the deliquescence point of both ammonium sulfate and sea salt (>70%); hence, a large fraction of the particles were growing by the diffusion of water vapor. Certain organic compounds will suppress this process (e.g. Lightstone et al., 2000) but when the RH remains higher than 80% for a period of time, most water soluble aerosol particles will begin to take up water regardless of the presence of these compounds (Hegg et al., 2001).

Diffusional growth also occurs during the interaction of particles with organic gases with low to medium vapor pressures. A number of the photochemically produced organic compounds are semi-volatile and readily diffuse to existing surface areas (Franklin et al., 2000; Claeyts et al., 2004). We can assess the relative rates of diffusional growth by comparing the trends in the particle properties that were measured with the CN counter, nephelometer, soot photometer, OPC and PPAH analyzer. Each of these instruments measures different but complementary properties that change as a result of growth by diffusion.

The CN counter measures the total number concentrations of particles larger than approximately 0.05 μm. The largest concentrations of particles are those in the nucleation, or Aitken size range, less than 0.1 μm, i.e. those produced by homogeneous or heterogeneous nucleation. Given the large amount of surface area in the city environment, it is unlikely that new particle formation is occurring anywhere except in the exhaust of motor vehicles or at the oil refinery where petroleum by-products are burned off and emitted from a number
of chimneys and large, open pools of burning material that were emitting grayish smoke. The density and color of the smoke indicate the presence of large concentrations of light absorbing particles.

The observed trends in CN concentration depend on the intensity of the emissions and the meteorological conditions that affect the rate of mixing and dilution. The growing boundary layer influences the dilution through turbulent mixing as does the introduction of maritime air with the onset of the sea breeze. Any changes in particle mass, whether by coagulation or diffusional growth, will have little effect on the total number concentration.

The size distribution measured by the OPC is for particles larger than 0.3 μm and less than 25 μm. This size range starts within the accumulation mode and ends in the coarse mode. Particles in the accumulation mode are generally those that have grown by diffusion and coagulation after they are initially produced by nucleation. The peak of the accumulation mode usually falls between 0.1 and 0.2 μm for urban aerosol particles (d’Almeida et al., 1991). Thus the OPC measures a large fraction of the accumulation mode particles and probably the majority of coarse mode particles, i.e. those produced from mechanical processes and whose peak number concentration is between 1 and 5 μm (d’Almeida et al., 1991). Some fraction of the particles from primary emissions will grow rapidly into the accumulation mode; hence, the trends in the total concentration measured by the OPC will follow those of the CN. This relationship changes, however, as particles continue to grow from sizes less than 0.3 μm, the lower threshold of the OPC, to larger sizes. This means that the ratio of OPC to CN concentrations should be small at the time of highest emissions and increase as these primary particles grow. This ratio is not affected by the CN and OPC concentrations and will decrease in the same proportion with no change as a result of dilution.

These features are best illustrated in the time series in Fig. 6 that is a single diurnal cycle. There are other days with similar trends but this particular day shows them most clearly. In particular, this was the only day when the DOAS clearly detected an elevated plume of SO2, as we discuss below. This is also a time period where there was a short power outage, as noted in Section 2, and is seen as a 1 h gap in the data from 19:00 to 20:00. The 5 min averages of particle concentrations, masses and column averaged SO2 concentration, shown in the times series in Fig. 6a to f, correspond to a 24 h period from 6:00 on day 168 to 6:00 on day 169. From 6:00 to 10:00 winds were low, less than 2 m s\(^{-1}\), and wind direction was highly variable (Fig. 6a, dashed line). The winds veered to the east for an hour before turning southerly and remaining from this direction until 21:00. From this time until 3:00, the winds were northerly before shifting to the east for the next 3 h.

The rapid increase in CN, PPAH and BC concentration at 7:00 (Fig. 6b, c and f) is a result of the morning traffic. The lack of data before this hour was the result of the data system failure mentioned earlier. The OPC concentration and \(B_{\text{scat}}\) also show an initial peak (Fig. 6c and e). The first peak in CN concentrations of 25,000 cm\(^{-3}\) is followed by a second maximum at 11:00 that is almost three times larger. This is also seen in the OPC concentration and \(B_{\text{scat}}\), however, the second maximum is not seen in the PPAH or BC.

The second \(B_{\text{scat}}\) peak is one and a half times larger than the first whereas the second OPC maximum is slightly less than the initial peak. The very high CN concentrations, lack of a correlation between PPAH and BC, and easterly winds indicate that these particles are not from local traffic emissions but are instead a result of particles that are coming from the refinery. The maximum CN concentration in the second peak is three times higher than earlier in the morning. The absence of BC and PPAH and high values of column-integrated SO2 (Fig. 6a) suggest that the composition of the particles was rich in non-volatile and/or semi-volatile OC, possibly with sulfur compounds. As seen in Fig. 1 (inset) the oil refinery is separated from the city by a line of hills. The winds are normally from the north such that the hills prevent the emissions from the refinery from reaching the research site. On this day, however, the winds remained easterly for a period sufficiently long to allow the emissions to reach the institute. This is clearly seen in the SO2 column measurements (Fig. 6a) whose initial peak corresponds to those observed in the CN, OPC and \(B_{\text{scat}}\) at the same time. In the late afternoon, when the winds were once again northerly, the local emissions are seen as large peaks in all the number and mass concentrations, as well as in \(B_{\text{scat}}\).

It was mentioned earlier that the CN concentrations never decrease to values that are representative of clean, marine air. This is underscored in Fig. 6f that shows that the CN are always above 5000 cm\(^{-3}\) during the period of the sea breeze. Similarly, neither the BC nor PPAH are completely removed and remain significantly higher than what would be expected from marine air masses. This suggests that the particles transported to the south during periods of northerly winds are returning with southerly winds. During the period shown in Fig. 6, the southerly wind continues for 7 h with an average...
velocity of $3 \text{ m s}^{-1}$. If this wind velocity and direction represent the average conditions, then air from 75 km to the south will eventually reach the research site. Since the concentrations of CN, PPAH and BC are almost constant during the 7 h period, this suggests that there is very little removal of the smallest particles, i.e. those that make up the largest fraction of CN, PPAH and BC. The lack of variability in these properties during this period of southerly flow also indicates that the particles have been homogeneously distributed over the Gulf of Tehuantepec to the south.

Another indication of the recycling of emissions is seen in the trends in SO$_2$ column concentration (Fig. 6a). Three hours after the initial 11:00 peak a secondary maximum appears with half the original magnitude. The winds are southerly hence the source of the SO$_2$ must be recirculated refinery emissions transported by the regional scale wind patterns. There is additional evidence for recirculated emissions in the OPC concentration time series (Fig. 6e) but not in the parameters which characterize fine PM, i.e. CN and PM1. Since the SO$_2$ measurements correspond to the
concentration observed in a column and the OPC traces sedimenting particles, we conclude that pollution carried by the return flow was higher aloft.

Another process that changes the characteristics of the aerosol particle population is the growth by diffusion of water vapor or precursor gases such as SO$_2$ and VOCs (e.g. Hegg et al., 1997; Kotchenruther et al., 1999). An example of growth by water vapor diffusion is seen in Fig. 6e, where the OPC concentration is seen to increase steadily after 12:00. This positive trend in concentration is a result of growth by particles whose diameters are initially below the 0.3 $\mu$m threshold of the OPC, but then grow to within its range of detection.

This is more clearly observed in Fig. 7a where the relationship between the OPC and CN is represented as a ratio of the two, calculated as an average every 30 min. This ratio represents the fraction of the total particle population that is larger than 0.3 $\mu$m and that depends on the underlying processes that modify the size distribution. As seen in Fig. 7d, these particles are about 4% of all particles during the period from 6:00 to 11:00; however, when the winds have shifted to southerly (Fig. 7a), this fraction increases as particles grow into the detectable range of the OPC. There is no new particle production during this period so the total particle concentration does not change. The ratio between the PM$_{1.0}$ and PM $>5$ $\mu$m (Fig. 7c) further underscores this growth process. The mass in the large particles remains almost constant while the mass in the 0.3 to 1 $\mu$m size range increases when the particles grow into the first size category of the OPC. The decrease in the ratios at 18:00, shown in Fig. 7c and d, is a result of fresh particles that arrive at the measurement site when the wind shifts back to northerly. At 18:00, the concentration of CN (Fig. 6f) and the mass of particles larger than 5 $\mu$m (Fig. 6c) begin to increase. Within an hour after

![Diagram](image_url)
these new emissions, however, the particles $<0.3 \, \mu m$ are once again seen to grow as reflected in the steady increase in the ratios of OPC to CN and PM$_{1.0}$ to PM $>5 \, \mu m$.

The ratio of the BC to PPAH, also averaged in 30 min segments, is probably dominated by gas-particle partitioning of PAH and changing of the primary source composition. Gas-particle partitioning of PAH reflects both adsorption (mostly to BC) and absorption (mostly to organic carbon) and is influenced by the particulate matter chemical composition, the nature of BC (i.e., availability of adsorption sites at the surface), aerosol water content and temperature (Lohmann and Lammel, 2004). BC and PPAH emissions from various emission sources, such as refinery and road traffic, vary widely (Masclet et al., 1986; EPA, 1995; Bond et al., 2004). Hence, varying source influences might explain changes in the ratios of BC to PAH. Another possibly interfering process would be aerosol aging as BC and PPAH differ in atmospheric lifetime. Combustion aerosols in aged air masses should be depleted in PAH due to effective photochemical decay; however, PPAH can undergo long-range transport (Behymer and Hites, 1988; Halsall et al., 2001), possibly because of diffusion into particulate organic matter and/or shell-like particle structures which both would prevent radical attack. As BC and PPAH at the site were from rather fresh emissions aerosol aging can be ruled out as a cause for the variation in BC to PPAH ratios. At 7:00, when the morning emissions are high, both the PPAH and BC increase and remain at an elevated value until the wind shifts to southerly. After this time they both decrease to a constant level until increasing again in the evening with northerly winds (Fig. 6a). From 7:00 to 11:00 and 19:00 to 22:00, the trend in the ratio of BC to PPAH is positive when winds are northerly and emissions are high. This signifies that the concentration of BC is increasing more rapidly than that of the PPAH. The BC concentration, like the CN, is sensitive only to the intensity of the primary particle source and to the degree of mixing with cleaner air. In the period after the winds shift to the south, the ratio of BC to PPAH decreases. This trend is not a result of dilution with the marine air as this would decrease the concentration of BC and PPAH in the same proportion. Hence, the reason that the BC to PPAH ratios decrease is that the BC concentration is remaining approximately constant while the PPAH is increasing by diffusional growth.

The rate of increase of the PPAH during the period of southerly wind is proportional to the trends in the ratios of BC to PPAH and OPC to CN. We assume that the CN and BC concentrations are from the same local source and that their values change only with the strength of the emissions and the degree of mixing with air of lower particle concentration. Secondly, we assume that changes in concentration due to mixing and dilution are independent of size or chemistry. With these assumptions, we expect a maximum in the BC vs. PPAH ratio during periods of high emissions and low winds. After this time the BC and PPAH concentrations will decrease by turbulent mixing as winds increase and the boundary layer grows. The change in the slope of BC vs. PPAH represents the increase in mass by diffusion and, as seen in Fig. 7c, this slope decreases from a maximum of 0.08 to a minimum of 0.02 over a period of 6 h. This is an estimated growth rate of approximately 12%/h.

During the same period, the slope of OPC vs. CN changed from 0.01 to 0.12, an estimated change in mass of approximately 15%/h. The increase in the slopes of OPC vs. CN results from particles that grow into the size range of the OPC and is related to diffusional growth from at least four sources of precursor gases: 1) PAH and other semi-volatile organic compounds (SOC), 2) water vapor, 3) SO$_2$ and 4) volatile organic compounds (VOC). Since the maximum PPAH was 50 ng m$^{-3}$, a mass concentration change in the 6 h period of 75% represents a change in diameter of less than 5%. This cannot account for the 90% shift in the concentration of particles that grew larger than 0.3 \, \mu m, as estimated from the slopes of OPC vs. CN. Growth by water vapor diffusion is a rapid process that will increase the diameter of particles more rapidly than that of PAH diffusion since the humidity was almost always greater than 70%. This does not discount the growth by condensation of trace gases; however, these will always be less abundant than water vapor.

5. Summary and conclusions

Trends in the physical and chemical properties of aerosol particles in a coastal city, near one of Mexico’s largest oil refineries, have been evaluated for a two-week period in June, 2004. From these observations, we are able to form a conceptual picture of how particles evolved in Salina Cruz:

1) The majority of particles observed at the research site within the city are emitted from local sources of combustion, i.e. from vehicles in the city and oil processing at the refinery.

2) The particle concentrations increase until solar heating forces the growth of the boundary layer and the subsequent dilution of the particle concentrations.
by turbulent mixing. During this period of northerly winds the emissions are transported to the south over the Gulf of Tehuantepec where they are diluted by marine air and dispersed into a more spatially homogeneous mixture.

3) Particles smaller than 0.1 \( \mu m \) are not removed by dry or wet deposition and some fraction of these increases in diameter by diffusional growth.

4) After the sea breeze commences, the particles that were transported to the south earlier in the day return to the city, lower in total number concentration, but with a shift in mass from the smaller to larger particles also through the process of diffusional growth.

5) When the wind velocities exceed 4 m s\(^{-1}\), significant concentrations of particles larger than 5 \( \mu m \) are produced, regardless of the wind direction. These particles are removed by inertial scavenging in precipitation or by dry deposition when the deposition rate exceeds the production rate.

The recirculation of anthropogenic emissions is an important air quality issue in this city and has been found to be a significant factor in other coastal urban areas. For example, studies in Athens, Greece have shown a similar pattern of recirculation where the mass concentrations of particles changed very little between sea and land breezes (Eleftheriadis et al., 1998; Klemm et al., 1998). Studies of pollutant gases on the southern coast of South Africa (Tyson and D’Abreton, 1998) and the western coast of Australia (Yimin and Lyons, 2003) also showed recirculation of pollutants that had originated from the land but returned with the sea breeze. In the case of Salina Cruz, the Gulf of Tehuantepec serves as a reservoir that stores the emissions from the city and refinery alike. The size of this reservoir will be limited by the extensions of the channeled northerly flow over the Isthmus (in east–west) and the height of the boundary layer (including the night-time residual layer). In many cases it will imply that pollution from the urban area of Salina Cruz accumulates during days (wet season) to weeks (dry season) in a finite volume until it is finally deposited by wash-out or deposition to the coastal area and waters. Such a meteorological setting enhances the human health risks of fine and ultrafine PM emissions and formation.

More generally, the situation at the Gulf of Tehuantepec is exemplary as a pattern of air pollution from coastal point sources that is being captured in limited areas. Similar conclusions on the influence of sea breeze on air pollution have been drawn for other urban coastal areas, mostly with emphasis on photo-oxidants under dry conditions (e.g. Athens: Clappier et al., 2000).

The city receives only a small fraction of the refinery’s direct emissions since the plume is elevated and there is a topographical barrier between the city and the refinery that restricts the flow when winds are from the north. The flow from the south recirculates many of these particles to the city after only the largest of them have been removed by deposition or precipitation. The physical and optical properties of the aerosol particles are only slightly modified during their period over the ocean. A larger cleansing effect for all size categories was expected during their diurnal transit, but only minor differences in the mass concentrations were observed between the land and sea breezes. Even though air masses could be transported about 100 km offshore, the processes responsible for the equilibrium size spectrum observed appear to be similar over land and over the ocean. It seems that the removal of small particles (below 1 \( \mu m \)) either by diffusional growth or by cloud processing reduces the mass concentration by a factor of 2 on average, during the period when particles are over the ocean. Note that the daytime hours is when the winds are from the ocean and the particle number and mass concentrations are lower, coinciding with increased dilution due to the deeper boundary layer. When strong winds are present, the mass concentration increases with size regardless of wind direction. This suggests that the mechanical production is larger than the removal for the large particle categories, and it is slightly more efficient during the land breeze, resulting in overall larger mass concentrations. Only during the intense precipitation events are larger mass concentrations observed in sea breeze conditions (in the 1–5 \( \mu m \) range) than during the land breeze.

The observations and analysis performed suggest that the local circulations play an important role in the transport of the aerosol particles that result in the observed size spectra at the surface. High resolution mesoscale modeling currently under way, and the topic of a companion paper, will provide further insight into these circulations and how they influence the transport and dispersal of pollutants in this complex environment.

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